# The Elemental Composition of $PM_{2.5}$ Collected During the Steubenville Comprehensive Air Monitoring Program

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# SCAMP

- Two-year comprehensive program for monitoring $PM_{2.5}$ and co-pollutants
- Steubenville, Ohio, and surrounding region
- May 2000 – May 2002
- Two major study components:
  - Indoor/Personal
    - Personal sampling of children and elderly volunteers
    - Indoor sampling in participants' homes
  - Outdoor
    - Participants' homes
    - Central site in Steubenville
    - Four remote sites located at cardinal compass points around Steubenville

# Today's Presentation

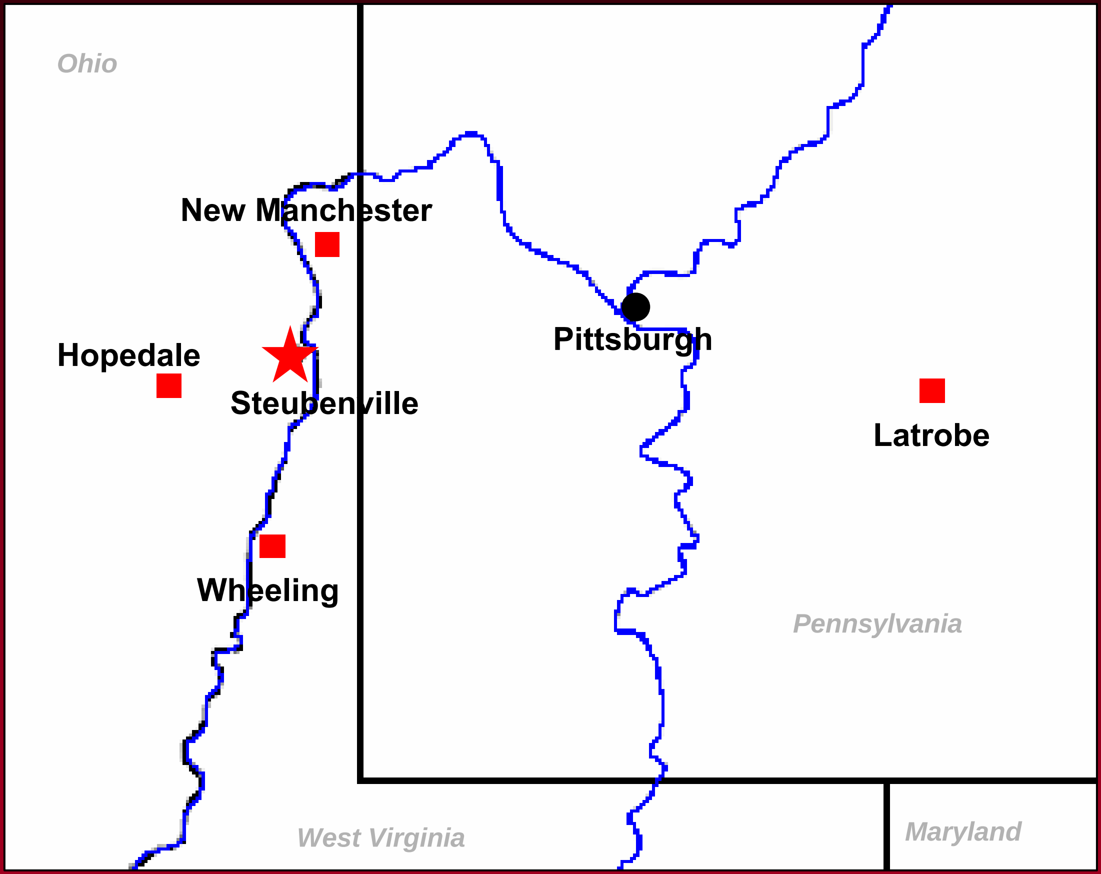
- SCAMP Outdoor Ambient Air Monitoring Network
  - Central Steubenville site
  - Four satellite sites
- Elemental Composition of the Water-Soluble $PM_{2.5}$ Fraction
  - Samples collected every 4th day using $PM_{2.5}$ FRM
  - Water-soluble components extracted ultrasonically using ultra-pure DI water with 2% IPA (wetting agent)
  - Elemental determination by Dynamic Reaction Cell ICP-MS (PerkinElmer ELAN 6100 DRC)
    - 21 elements of interest
    - Ge and In used as internal standards to correct for drift
    - Results validated using NIST 1643d

# Studies of $PM_{2.5}$ Elemental Composition in Steubenville

- Koutrakis and Spengler (1987)
  - Elemental data collected in 1984 (XRF)
  - SRFA applied to identify six possible sources of $PM_{2.5}$
- Laden, Neas, Dockery, and Schwartz (2000)
  - Elemental data collected from 1979 through late 1980s (XRF)
  - Investigated associations among mortality and $PM_{2.5}$ sources
- SCAMP
  - Reflects changes in Steubenville over past 15+ years
  - DRC ICP-MS
  - Water-soluble and "total" (acid-digestible) $PM_{2.5}$ fractions

**► SIP Development, Health Effects**

# Outdoor Ambient Monitoring Sites



# Outdoor Ambient Monitoring Sites

# ICP-MS

- Sensitivity
  - ppb to ppt for many trace elements of interest
  - Generally better than XRF
- Capable of determining multiple isotopes
- Destructive technique
  - Can compare water-soluble vs. acid-digestible fractions

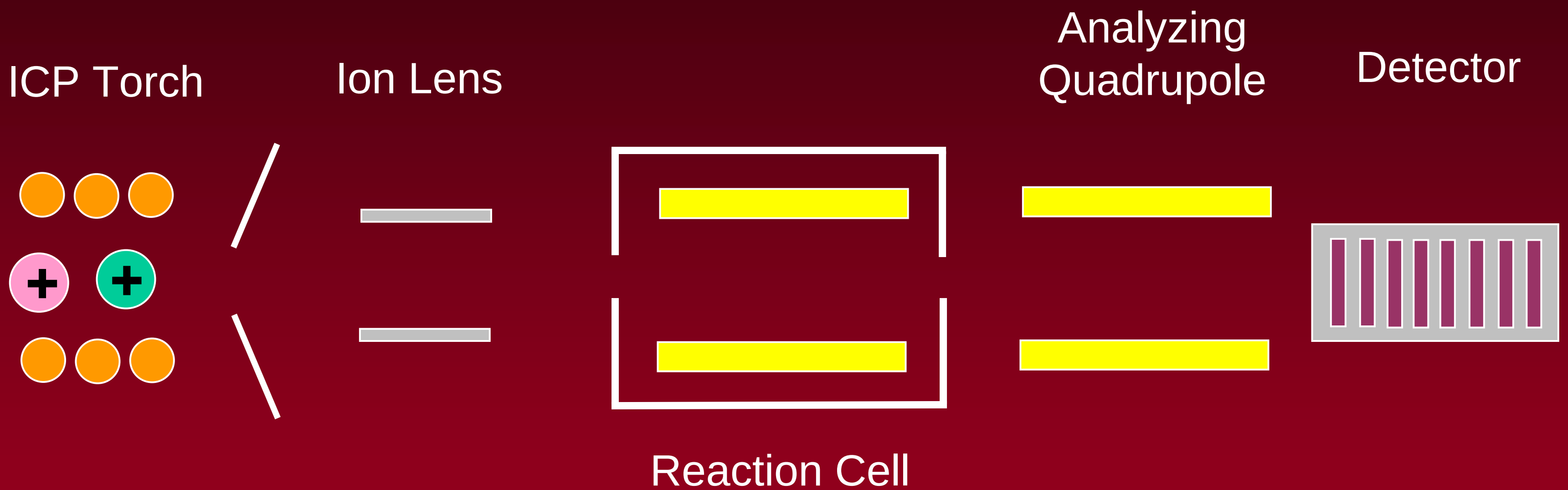
**Major Limitation: Interferences**

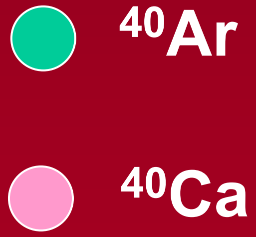
| Isobaric | Polyatomic |
| --- | --- |
| $^{40}Ar^{+} \Leftrightarrow {}^{40}Ca$ | $^{40}Ar^{35}Cl^{+} \Leftrightarrow {}^{75}As$ |

Affected Species Include:

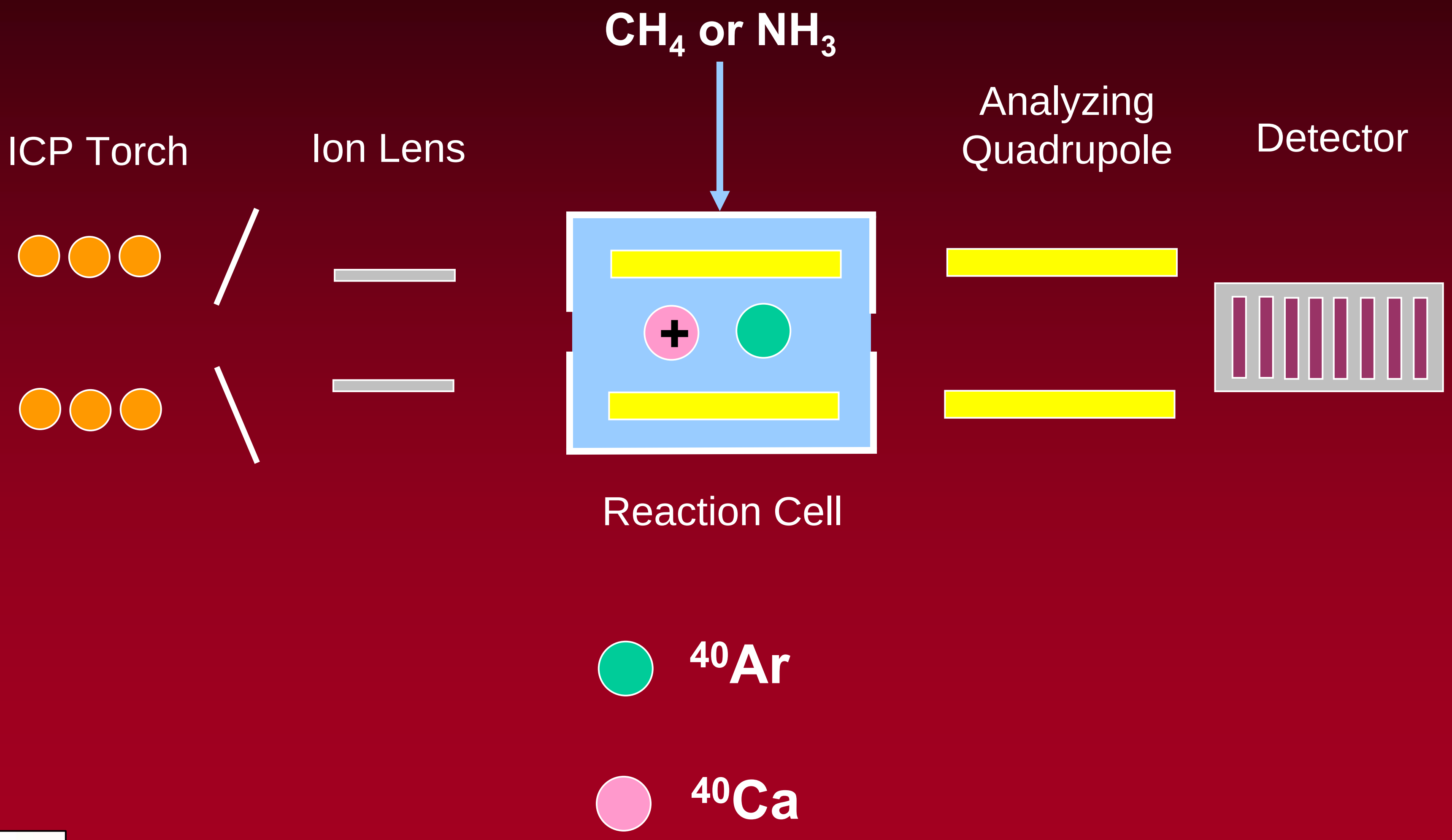
$^{28}Si$, $^{39}K$, $^{40}Ca$, $^{51}V$, $^{52}Cr$, $^{56}Fe$, $^{75}As$, $^{80}Se$

# Dynamic Reaction Cell ICP-MS

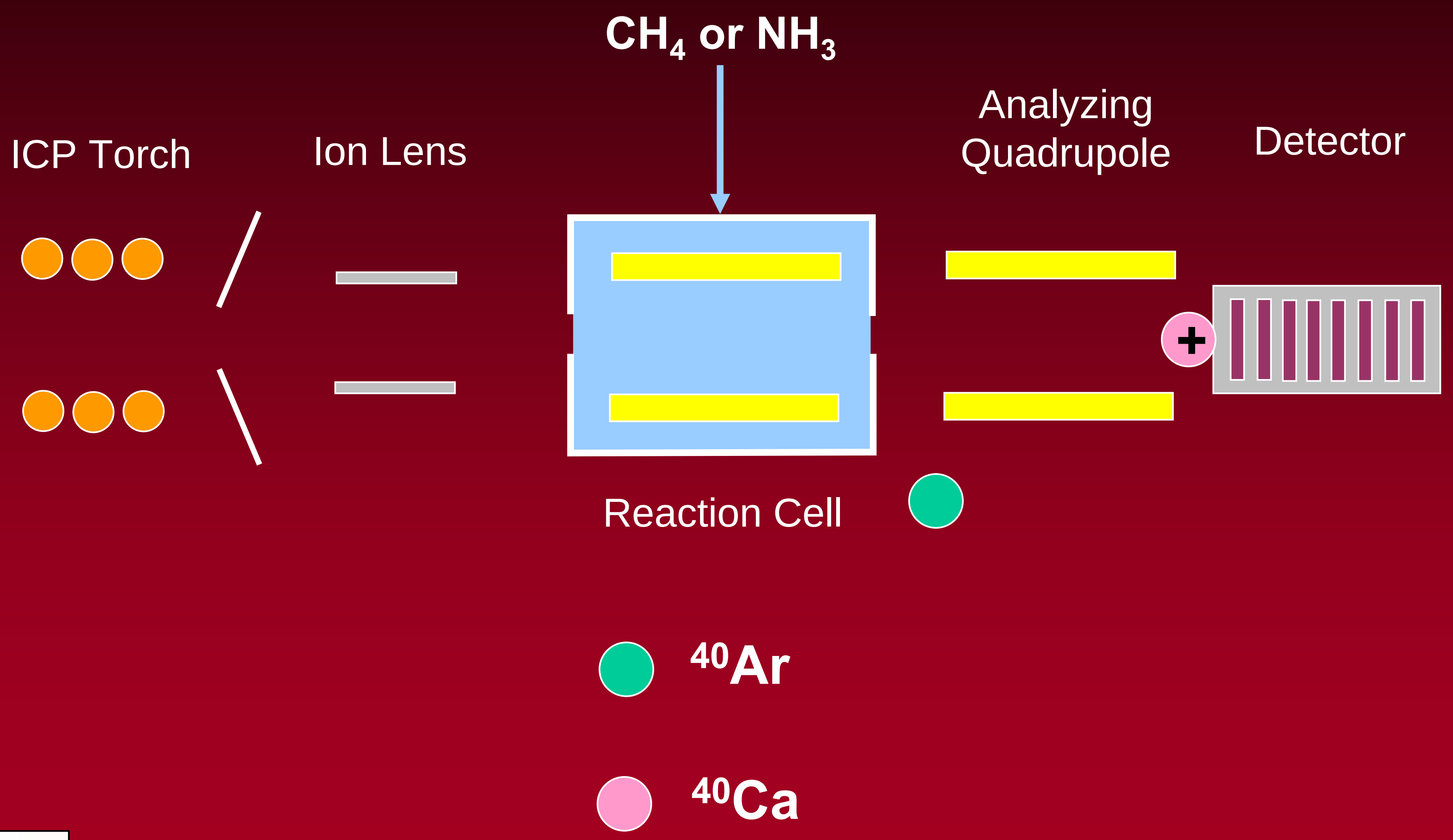


# Dynamic Reaction Cell ICP-MS



# Dynamic Reaction Cell ICP-MS



# DRC ICP-MS Detection Limits

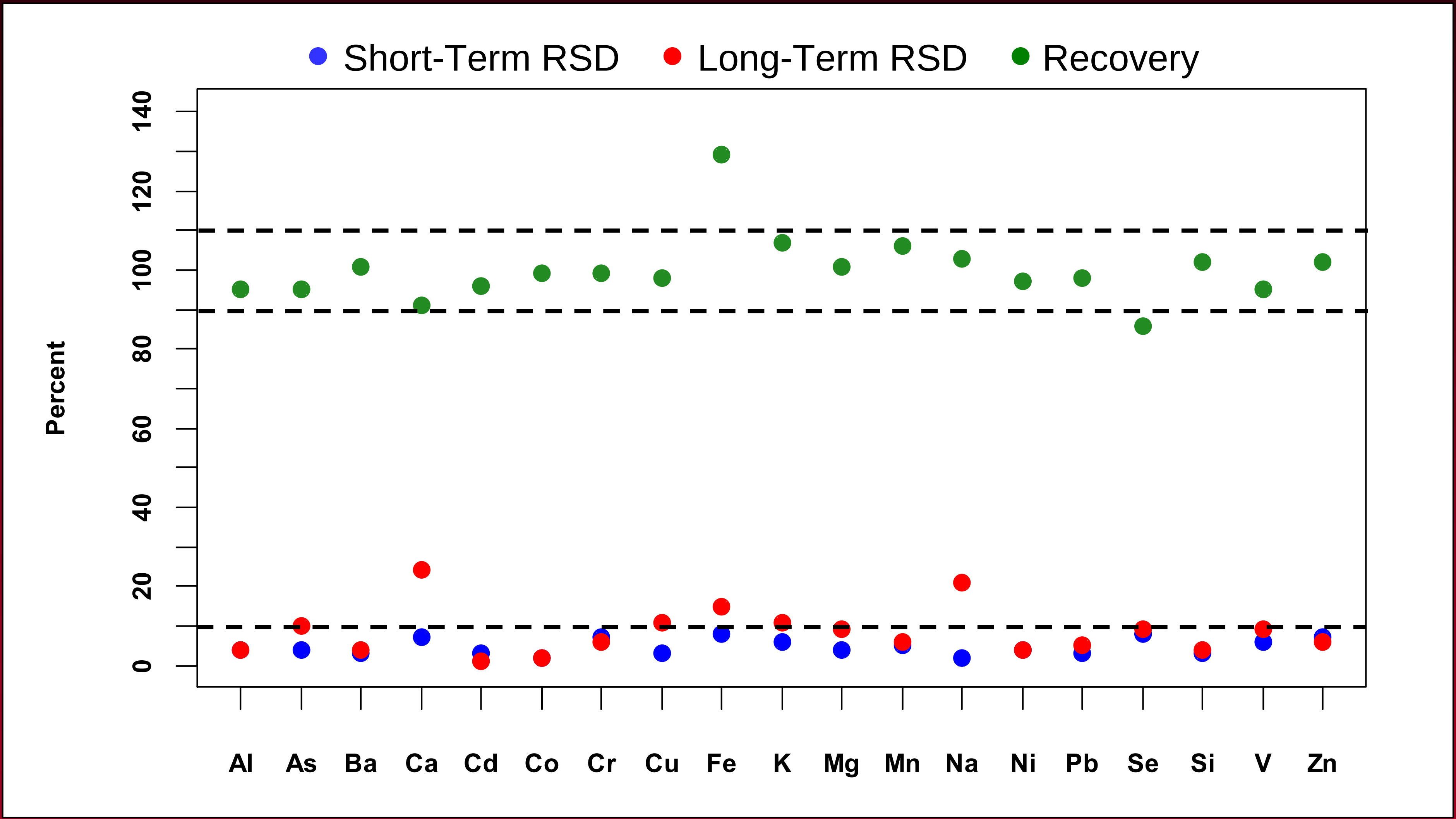
| | DL (ng/m$^3$) | % Obs < DL |
|---|---|---|
| **Al** | 0.1 | 0 |
| **As** | 0.04 | 0 |
| **Ba** | 0.01 | 0 |
| **Ca** | 1,3,12,27 | 0 |
| **Cd** | 0.01 | 0 |
| **Co** | 0.002 | 1 |
| **Cr** | 0.03,2.16 | 79 |
| **Cu** | 0.04 | 0 |
| **Fe** | 0.2,1.8,5.2 | 4 |
| **K** | 0.3,0.4,0.5,69 | 5 |

| | DL (ng/m$^3$) | % Obs < DL |
|---|---|---|
| **Mg** | 0.1,0.2 | 0 |
| **Mn** | 0.8 | 9 |
| **Na** | 1,2 | 0 |
| **Ni** | 0.1,0.2 | 2 |
| **Pb** | 0.1 | 1 |
| **Se** | 0.05,0.26 | 1 |
| **Si** | 6,7,25 | 3 |
| **Sn** | 0.021 | 5 |
| **V** | 0.08 | 3 |
| **Zn** | 0.2 | 0 |

**High Blank Concentrations**

# DRC ICP-MS Performance

## Based on Determinations of NIST 1643d (10x Dilution)



# Summary Statistics

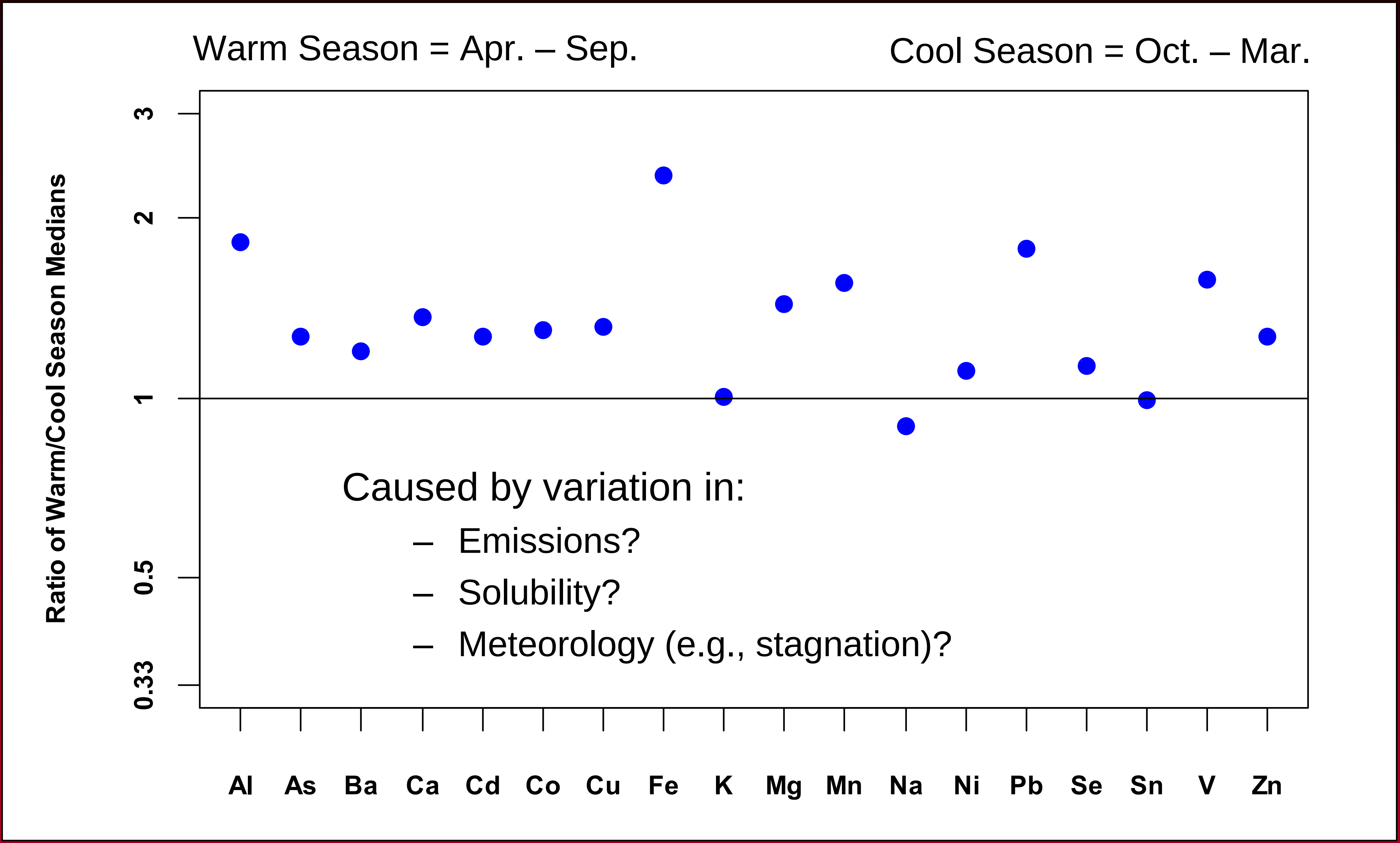
## Elements in the Water-Soluble Fraction at Steubenville

| | Mean ($ng/m^3$) | Max ($ng/m^3$) | RfC[a] ($ng/m^3$) |
|---|---|---|---|
| **Al** | 18.8 | 124.3 | |
| **As** | 2.37 | 18.27 | 30 |
| **Ba** | 1.9 | 8.6 | |
| **Ca** | 85 | 310 | |
| **Cd** | 0.50 | 7.16 | 20 |
| **Co** | 0.038 | 0.132 | 100 |
| **Cu** | 3.2 | 26.4 | |
| **Fe** | 19.6 | 136.4 | |
| **K** | 99 | 314 | |

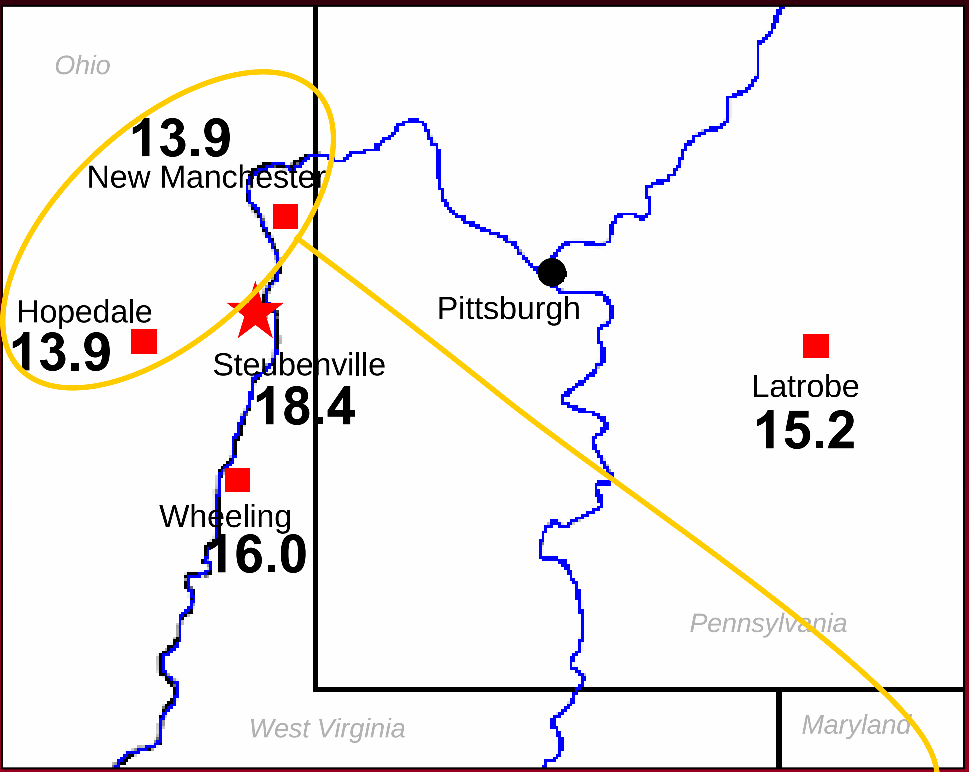
| | Mean ($ng/m^3$) | Max ($ng/m^3$) | RfC[a] ($ng/m^3$) |
|---|---|---|---|
| **Mg** | 30 | 321 | |
| **Mn** | 7.8 | 41.3 | 50 |
| **Na** | 90 | 501 | |
| **Ni** | 0.7 | 6.9 | 50 |
| **Pb** | 8.9 | 121.6 | 1,500 |
| **Se** | 4.71 | 33.91 | 20,000 |
| **Sn** | 0.215 | 2.354 | |
| **V** | 1.04 | 7.80 | |
| **Zn** | 55.6 | 435.5 | |

[a]Based on USEPA, US ATSDR, or CalEPA

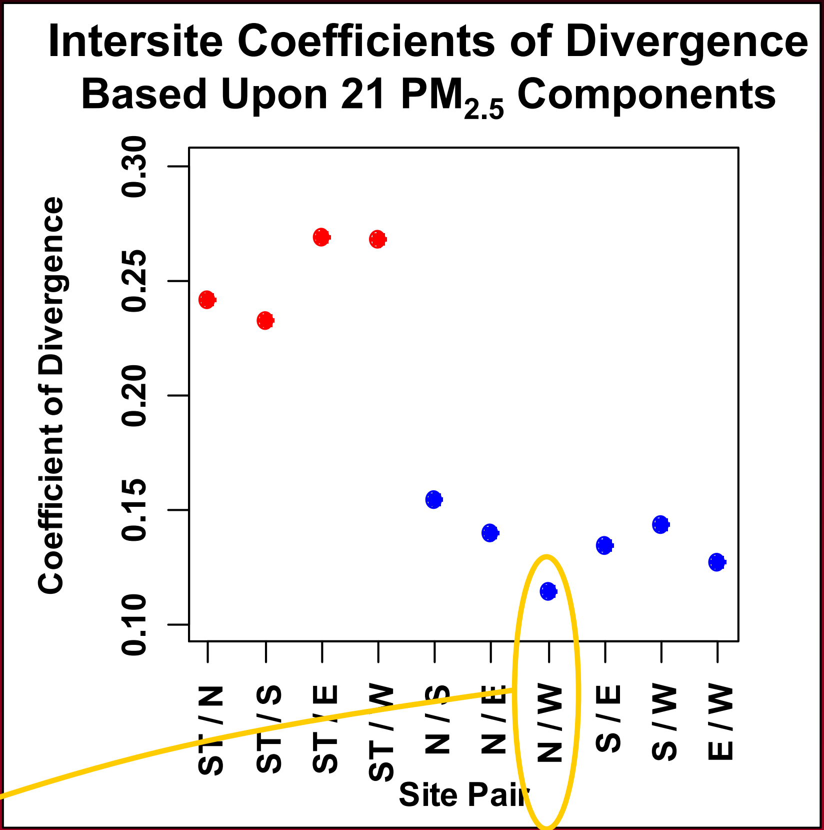
# Warm vs. Cool Season Concentrations



# Spatial Variability




Less Similar




**"Background" Sites**

$$CD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}}\right)^2}$$

# Local Source Contributions

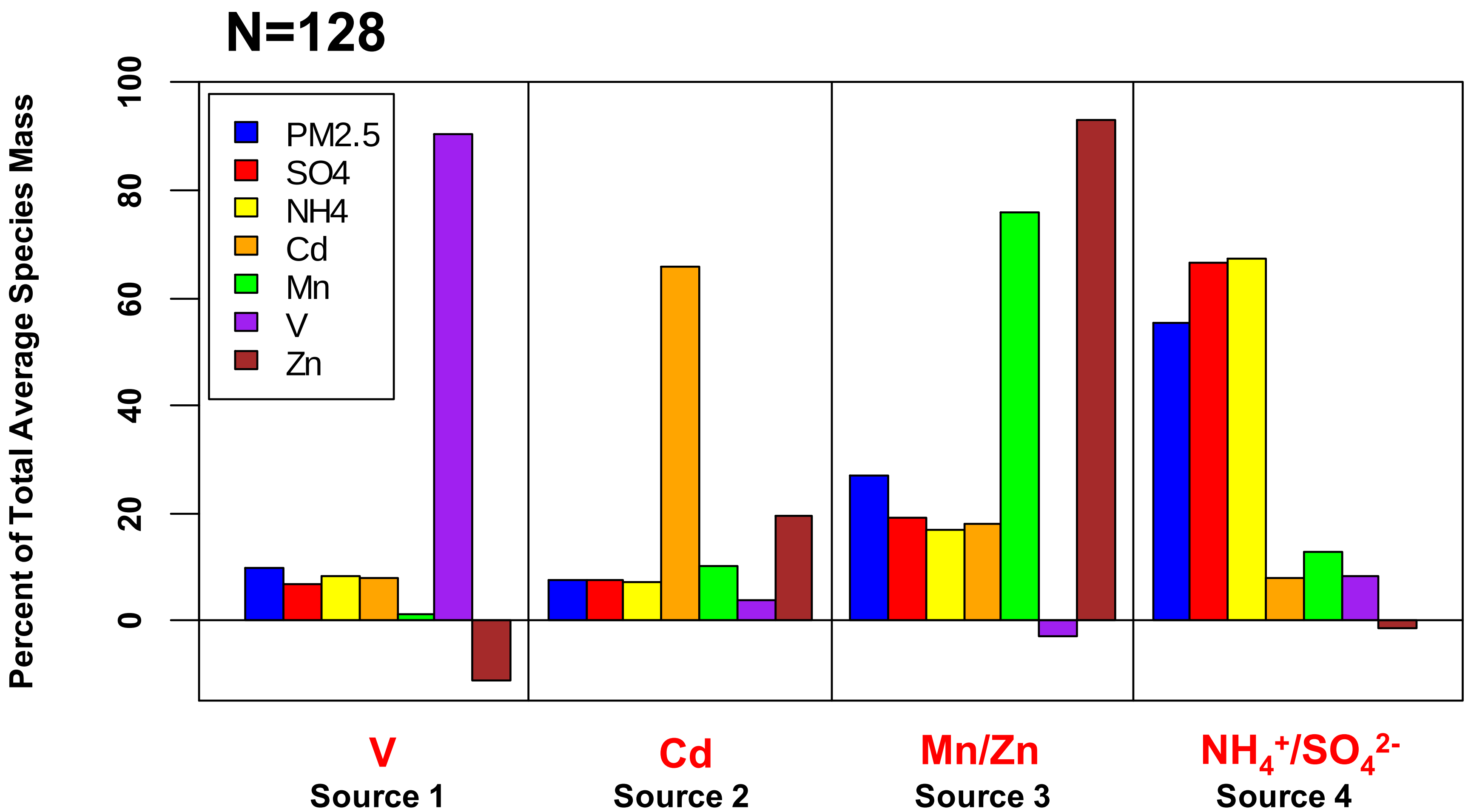
## Elements in the Water-Soluble Fraction

| | % ST > BG | Loc. (ng/m$^3$) | Loc. (% of BG) |
|---|---|---|---|
| Al | 71 | 4.8 | 49 |
| As | 73 | 0.66 | 43 |
| Ba | 79 | 0.7 | 65 |
| Ca | 73 | 28 | 46 |
| Cd | 71 | 0.10 | 31 |
| Co | 43 | -0.004 | -10 |
| Cu | 59 | 0.7 | 31 |
| **Fe** | **71** | **11.8** | **106** |
| K | 59 | 16 | 21 |

| | % ST > BG | Loc. (ng/m$^3$) | Loc. (% of BG) |
|---|---|---|---|
| **Mg** | **79** | **18** | **145** |
| **Mn** | **83** | **4.5** | **154** |
| Na | 73 | 19 | 32 |
| Ni | 47 | 0.1 | 11 |
| Pb | 69 | 3.1 | 78 |
| Se | 54 | -0.44 | -9 |
| Sn | 38 | -0.017 | -9 |
| V | 63 | 0.44 | 66 |
| **Zn** | **75** | **25.5** | **140** |

# UNMIX Source Apportionment Results

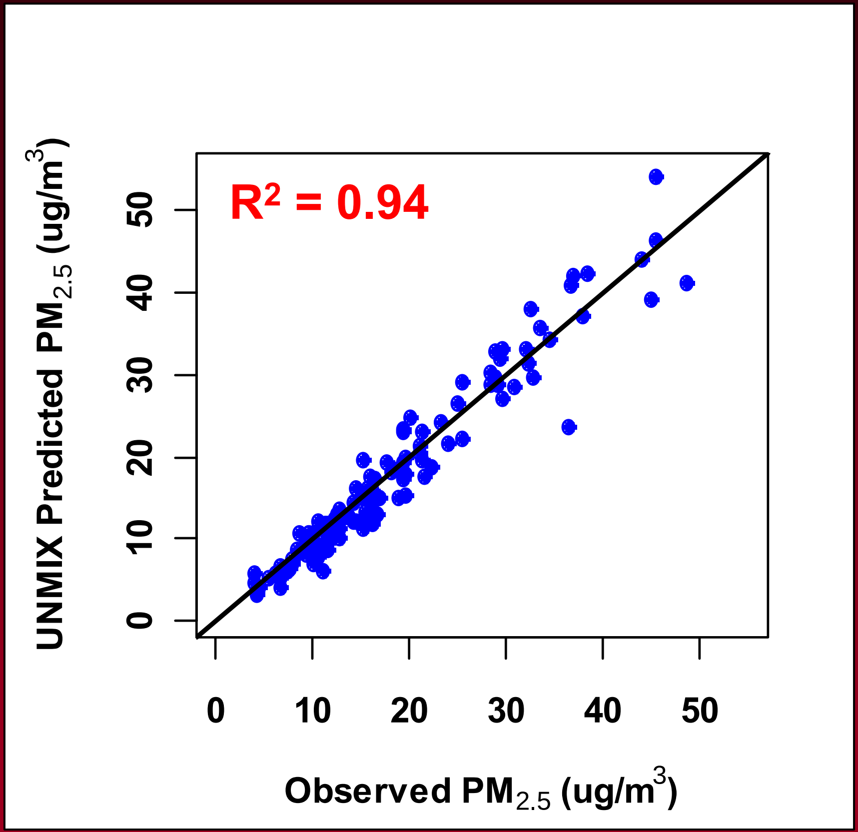
## Steubenville Site




| 1.7 µg/m³ (9.8%) | 1.3 µg/m³ (7.5%) | 4.7 µg/m³ (27.2%) | 9.6 µg/m³ (55.5%) |
|---|---|---|---|

# UNMIX Source Apportionment Results (2)

## Steubenville Site



# A Closer Look at Source 3

$$[Mn]_{TOT} = 1.71[Mn]_{WS} + 0.61$$
$$[Zn]_{TOT} = 1.02[Zn]_{WS} + 21.95$$

$\rightarrow$ Source 3 Mn/Zn = 0.14

$\rightarrow$ Source 2 Mn/Zn = 0.06

**2001 TRI (Air Emissions) in Jefferson County, OH**

Mn/Zn for primary metals industry = 0.16

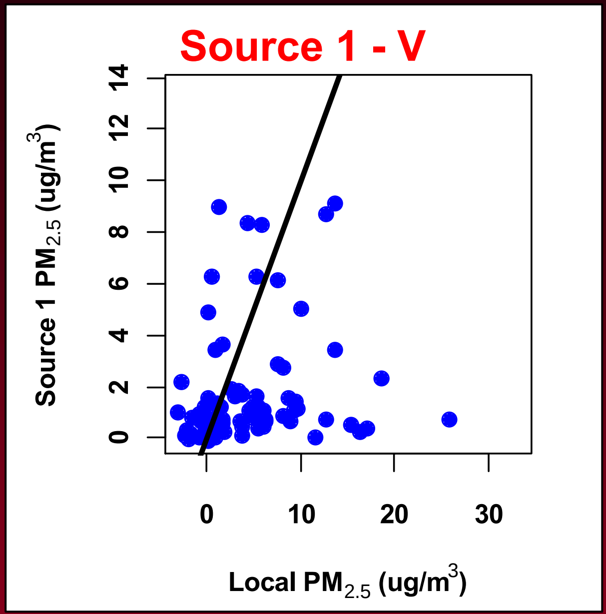
Mn/Zn for electric utilities = 0.42

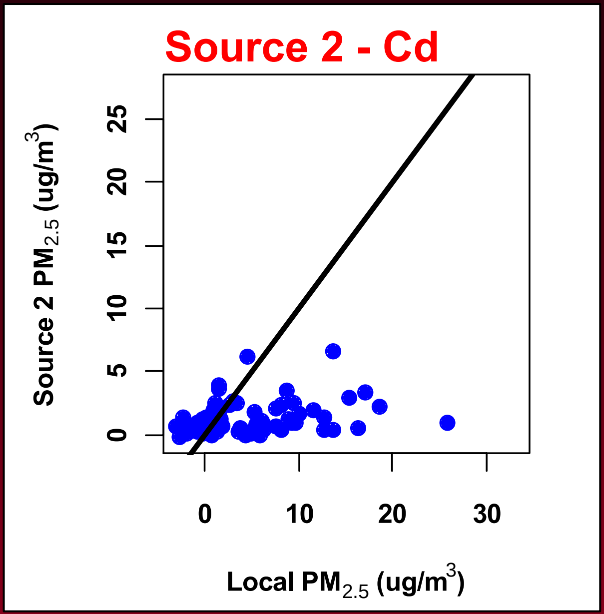
**Koutrakis and Spengler (1987)**

Mn/Zn for iron and steel production = 0.15

# UNMIX-Derived Source Contributions vs. Local Source Contributions

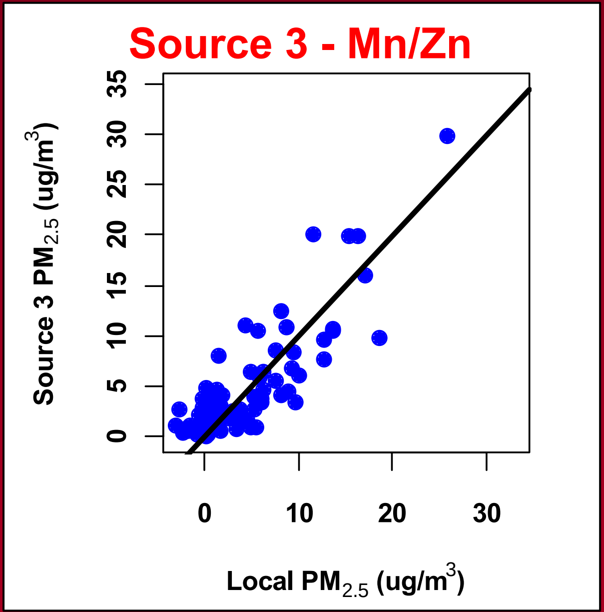
$r_s = 0.37$

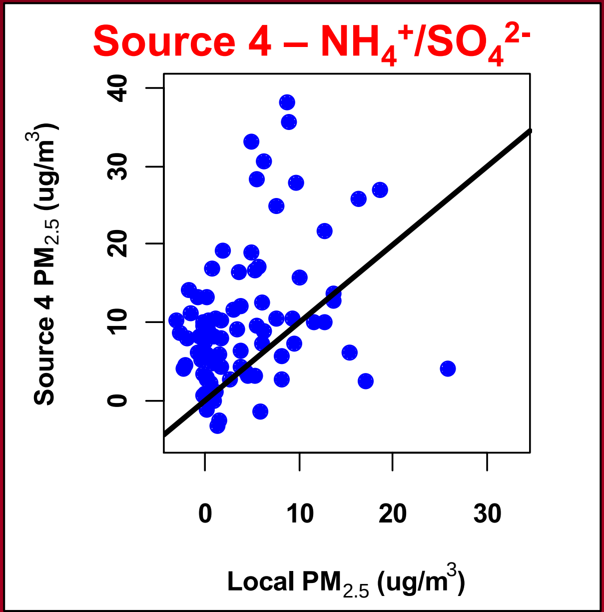



$r_s = 0.36$

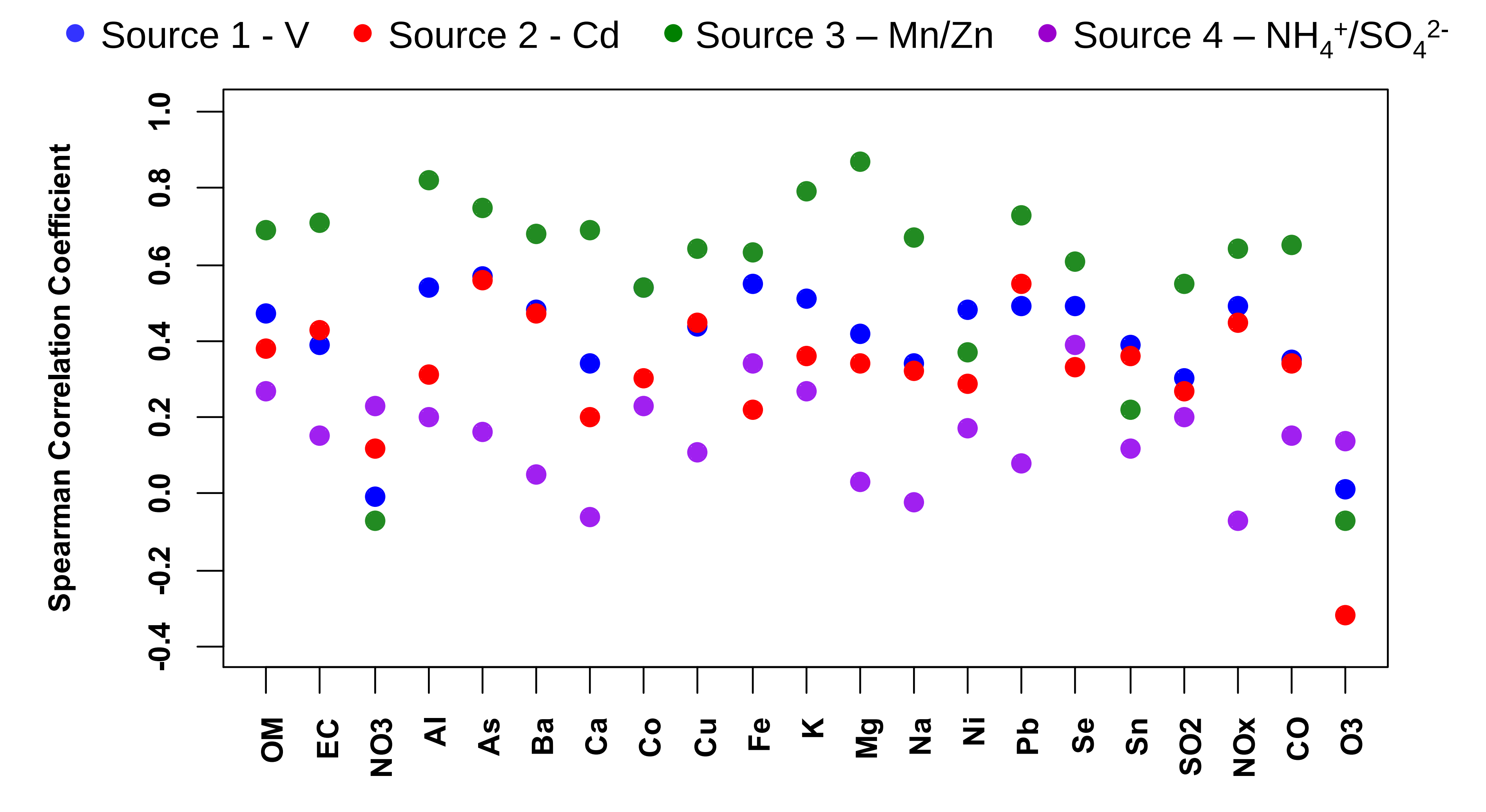
$r_s = 0.78$




$r_s = 0.31$

# Correlations – UNMIX-Derived Source Contributions vs. $PM_{2.5}$ Components, Gases



# Summary

- DRC ICP-MS exhibited adequate performance to determine 18 elements of interest in the water-soluble $PM_{2.5}$ fraction.
  - Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, Sn, V, Zn
- Average ambient air concentrations of these 18 elements collectively account for ~ 0.4 µg/m$^3$ (2%) of Steubenville's total $PM_{2.5}$ mass concentration.
- Mean concentrations of As, Cd, Co, Pb, Mn, Ni, and Se in the water-soluble $PM_{2.5}$ fraction were 1/5 to 1/1000 as much as chronic inhalation reference concentrations.
  - No RfCs available for key elements such as Cu, Zn, Fe, V
- Fifteen of the 18 elements studied had higher median concentrations during the warm season than during the cool season.
  - Same trend as total $PM_{2.5}$, $SO_4^{2-}$
  - Possible causes still being explored

# Summary

- Local sources in Steubenville contribute appreciably to concentrations of a number of elements in the water-soluble $PM_{2.5}$ fraction.
  - Average concentrations of Fe, Mg, Mn, and Zn were more than twice as high at Steubenville as at background sites
- Application of UNMIX to ionic and elemental data from water-soluble $PM_{2.5}$ yielded a 4-source solution.
  - $NH_4^+/SO_4^{2-}$ source accounted for ~55% of total $PM_{2.5}$ mass
  - Mn/Zn source accounted for ~27% of total $PM_{2.5}$ mass
    - Mn/Zn ratio similar to TRI ratio for primary metals industry
    - Highly correlated with local source contributions estimated from measured data
    - More strongly correlated with OM, EC, Al, As, Ba, Ca, Co, Cu, Fe, K, Mg, Na, Pb, Se, $SO_2$, $NO_x$, and CO than the other three sources
  - Cd and V sources were characterized by larger uncertainties; will be studied further using acid-digestible elemental data

# Funding

U.S. DOE – National Energy Technology Laboratory

Ohio Coal Development Office

Electric Power Research Institute

American Petroleum Institute

National Mining Association

American Iron and Steel Institute

Edison Electric Institute

National Institute of Environmental Health Sciences

U.S. Environmental Protection Agency

CONSOL Energy Inc.

# Participating Groups

CONSOL Energy Inc. R&D

Harvard School of Public Health

Franciscan University of Steubenville

Ohio University

Wheeling Jesuit University

St. Vincent College

Optimal Technologies

Air Quality Sciences, Inc.

Control Analytics, Inc.

# Publications

- Connell et al. The Steubenville Comprehensive Air Monitoring Program (SCAMP): Overview and Statistical Considerations; *J. Air & Waste Manage. Assoc.* **2005**, *55*, 467-480.

- Connell et al. The Steubenville Comprehensive Air Monitoring Program (SCAMP): Associations Among $PM_{2.5}$, Co-Pollutants, and Meteorological Conditions; *J. Air & Waste Manage. Assoc.* **2005**, *55*, 481-496.

- Connell et al. The Steubenville Comprehensive Air Monitoring Program (SCAMP): Analysis of Short-Term and Episodic Variations in $PM_{2.5}$ Concentrations Using Hourly Air Monitoring Data; *J. Air & Waste Manage. Assoc.* **2005**, *55*, 559-573.